Hyperbranched Poly(phenylenesilolene)s: Synthesis, Thermal Stability, Electronic Conjugation, Optical Power Limiting, and Cooling-Enhanced Light Emission

Junwu Chen, Han Peng, Charles C. W. Law, Yuping Dong, Jacky W. Y. Lam, Ian D. Williams, and Ben Zhong Tang*

Department of Chemistry, Center for Display Research, Institute of Nano Science and Technology, and Open Laboratory of Chirotechnology,[†] Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

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ABSTRACT: Silole-containing hyperbranched polyphenylenes (1) are synthesized, which exhibit high thermal stability, extended electronic conjugation, excellent optical power limiting performance, and novel cooling-enhanced photoluminescence. The homopolycyclotrimerization of 1,1-diethynyl-2,3,4,5-tetraphenylsilole (2) and its copolycyclotrimerizations with 1-octyne catalyzed by TaCl$_5$–Ph$_4$Sn proceed smoothly at room temperature and produce completely soluble polymers in high yields (up to ~85%). The molecular structures of 1 are characterized by spectroscopic analyses. The thermal stability of 1 is evaluated by thermogravimetric analyses, which detect virtually no weight losses when the polymers are heated to ~300 °C. The hyperbranched polyphenylenes are electronically conjugated, as suggested by their strong absorption in the visible spectral region (λ_{max} ~ 520 nm). Because of this extended electronic conjugation, polymers 1 are nonlinear optically active and strongly attenuate the optical power of intense laser pulses, whose optical limiting performances are superior to that of C$_{60}$, the best-known optical limiter. The photoluminescence of the polymers is dramatically enhanced by cooling their solutions to low temperatures. This unique phenomenon of cooling-enhanced emission is probably caused by the restricted intramolecular rotations of the phenyl rings upon the axes of the single bonds linked to the silole cores at the cryogenic temperatures.

Introduction

Silacyclopentadienes or siloles are a group of organometallic molecules that possess novel electronic and optical properties. The five-membered silacyclics exhibit, for example, high electron acceptability[1] and fast electron mobility.[2] We have recently observed a novel phenomenon of *aggregation-induced emission* (AIE) in this group of molecules: the siloles are practically nonluminescent when molecularly dissolved in good solvents but become highly emissive when aggregated into nanoclusters or fabricated into thin solid films.[3–5] The AIE effect greatly boosts the quantum yields of photoluminescence of the siloles (by more than 300-fold), turning them from faint fluorophores into strong emitters. Utilizing this AIE property, we have fabricated silole-based light-emitting diodes, which exhibit truly outstanding electroluminescence performance. A diode of 1,1,2,3,4,5-hexaphenylsilole (HPS; Chart 1), for example, radiates brilliantly (luminance up to ~60 000 cd/m^2), while that of 1-methyl-1,2,3,4,5-pentaphenylsilole (MPS) shows an extremely high external quantum efficiency (η_{EL} = 8%),[3,4] reaching the theoretical limit for a light-emitting diode based on a singlet emitter.[6,7]
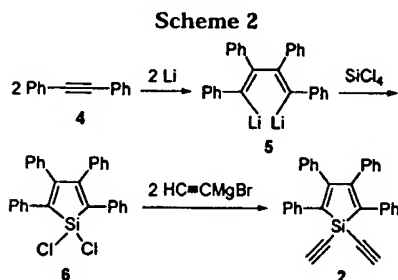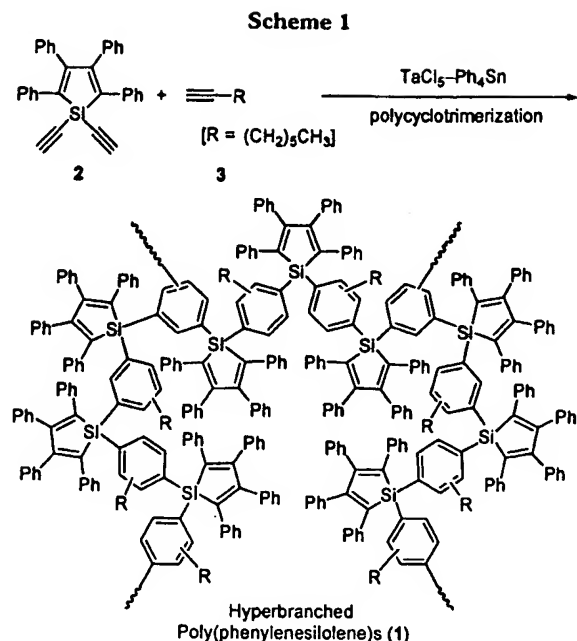
We are interested in incorporating the silole chromophores into conjugated polymers in an effort to create new materials that are easily processable and have useful optoelectronic properties. In our previous work, we designed and synthesized silole-containing polyacetylenes, examples of which are given in Chart 2.[8] All

Chart 1

HPS   MPS

Chart 2

PS9PA   PS9A   PSA
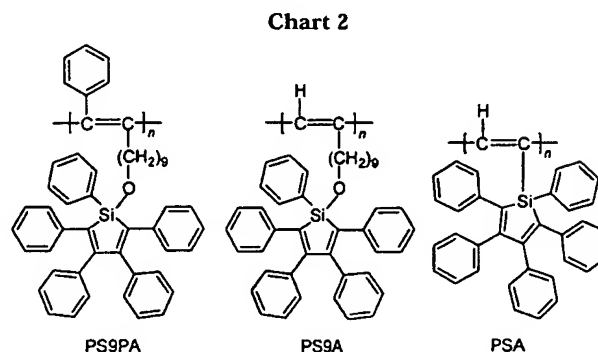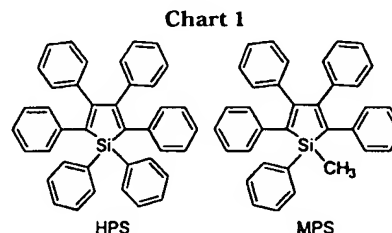
of the poly(silolylacetylene)s are completely soluble in common solvents and are readily processable. Like their silole parents, the polymers are nonemissive in molecularly dissolved solutions. When poor solvents are added into the dilute solutions, the polymers aggregate into nanosize particles. The nanoaggregates of poly{11-[(1,2,3,4,5-pentaphenylsilolyl)oxy]-1-phenyl-1-undecyne} (PS9PA) and poly{11-[(1,2,3,4,5-pentaphenylsilolyl)oxy]-1-undecyne} (PS9A) are highly luminescent (AIE-active); in contrast, those of poly(1,2,3,4,5-pentaphenylsilolylacetylene) (PSA) are nonradiative (AIE-

Scheme 1

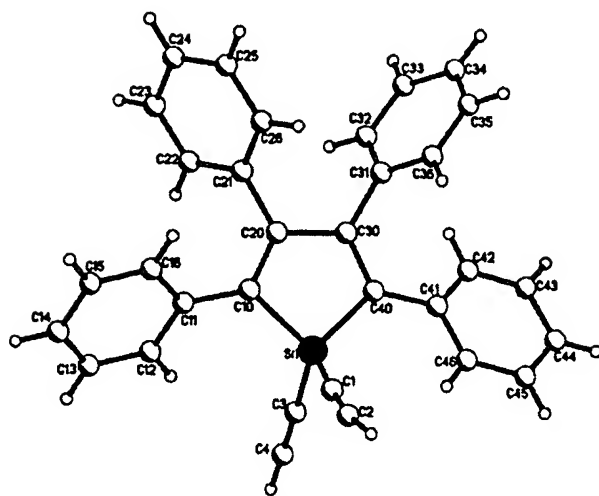Hyperbranched
Poly(phenylenesilolene)s (1)

Scheme 2

Figure 1. ORTEP drawing of 2 with atom-labeling scheme for Table 2.

Table 1. Summary of Crystal Data and Intensity Collection Parameters for 1,1-Diethynyl-2,3,4,5-tetraphenylsilole (2)

empirical formula	$C_{32}H_{22}Si$
mol wt	434.59
crystal dimensions, mm	0.35 × 0.25 × 0.15
crystal system	triclinic
space group	$P\text{-}1$
unit cell constants	
a, Å	11.1276(8)
b, Å	12.5644(9)
c, Å	18.1209(13)
α, deg	106.305(3)
β, deg	99.974(3)
γ, deg	90.573(3)
V, Å^3	2390.3(3)
Z	4
D_{calcd}, g cm^{-3}	1.208
F_{000}	912
temp, K	100(2)
radiation, λ, Å	Mo Kα, 0.710 70
μ(Mo Kα) mm^{-1}	0.116
$2\theta_{max}$, deg [completeness]	50 [98.5%]
no. of collected reflns	12 129
no. of unique reflns [R(int)]	8283 [0.0329]
data/restraints/parameters	8283/0/599
R_1, wR_2 [obs $I > 2\sigma(I)$]	0.0474, 0.0746
R_1, wR_2 (all data)	0.0718, 0.0816
goodness of fit, S	0.883
residual peak/hole e$^-$ Å^{-3}	0.333/−0.319
transmission ratio	1.0/0.81

inactive). The photoluminescence efficiencies of PS9(P)A can be boosted by cooling their molecularly dissolved solutions (*cooling-enhanced emission*).

In the work discussed above, the silole-containing linear polyacetylenes are synthesized by metathesis polymerization of acetylenes (or monoynes).[8,9] In this work, we intend to generate nonlinear or three-dimensional silole polymers by incorporating the silole rings into hyperbranched polyarylene structures via cyclotrimerization of diacetylenes (or diynes). We utilized the diyne polycyclotrimerization route we recently developed[10,11] and succeeded in the synthesis of hyperbranched poly(phenylenesilolene)s 1 (Scheme 1). All of the polymers are completely soluble in common organic solvents due to their highly branched molecular structures. The polymer solutions are somewhat luminescent but are completely AIE-inactive. The luminescence of the hyperbranched polymers can, however, be enhanced by cooling their solutions to low temperatures.

Results and Discussion

Monomer and Polymer Syntheses. To make silole susceptible to diyne polycyclotrimerization, we attached two ethynyl groups to the 1,1-position of the silacyclopentadiene ring. Following the synthetic route shown in Scheme 2, we prepared a silolyldiyne monomer, 1,1-diethynyl-2,3,4,5-tetraphenylsilole (2). Lithiation of tolane (4) gives 1,4-dilithiotetraphenylbutadiene (5), the cyclization of which with silicon(IV) chloride[12] yields 1,1-dichloro-2,3,4,5-tetraphenylsilole (6).[8] Its nucleophilic substitution with a Grignard reagent,[13] ethynylmagne-

sium bromide, leads to the formation of the desired monomer 2.

The silolyldiyne (2) gives satisfactory analysis data (see Experimental Section for details). Its crystal structure was studied by X-ray diffraction, and the crystal and diffraction data are summarized in Table 1. Crystals of 2 belong to the triclinic system, space group $P\text{-}1$, with two molecules per asymmetric unit. The structure refinement proceeded smoothly to final discrepancy indices $R_1 = 4.7\%$ and $wR_2 = 8.16\%$ for data to $2\theta = 50°$. The two independent molecules in the asymmetric unit have similar molecular geometries but differ slightly in the dispositions of the twist angles of the phenyl rings with respect to the silacyclopentadiene plane. A plot of one molecule in the asymmetric unit with labeling scheme is displayed in Figure 1, and the selected geometric parameters are listed in Table 2.

Search of the Cambridge Structural Database (CSD 5.23) found 51 records for silacyclopentadienes, and the

Table 2. Geometrical Parameters for Crystal of 1,1-Diethynyl-2,3,4,5-tetraphenylsilole (2)

Bond Length (Å)

Si1−C10	1.862(2)	Si1−C40	1.853(2)	Si1−C1	1.824(2)	Si1−C3	1.808(2)
C10−C20	1.353(3)	C20−C30	1.503(3)	C(30)−C(40)	1.365(3)		
Si1−C1	1.824(2)	Si1−C3	1.808(2)				
C1−C2	1.182(3)	C3−C4	1.185(3)				

Bond Angle (deg)

C10−Si1−C40	93.86(9)	Si1−C10−C20	106.45(15)
C10−C20−C30	116.68(18)	Si1−C10−C11	125.69(15)
C10−C20−C21	123.49(19)	C1−Si1−C3	106.99(10)
Si1−C1−C2	176.7(2)	Si1−C3−C4	176.3(2)

Torsion Angle (deg)

Si1−C10−C20−C30	3.3(2)	C10−C20−C30−C40	0.5(3)
C16−C11−C10−C20	−44.6(4)	C42−C41−C40−C30	−31.8(3)
C32−C31−C30−C20	−66.8(3)	C26−C21−C20−C30	−58.2(3)

Table 3. Synthesis[a] and Properties of Hyperbranched Poly(phenylenesilolene)s 1

no.	feed ratio [3]/[2][b]	polymer yield (%)	$M_w{}^c$ (Da)	$M_w/M_n{}^c$	$A_{pen}/A_{ph}{}^d$	$T_d{}^e$ (°C)	$F_L{}^f$ (mJ/cm²)	$F_{t,m}/F_{i,m}{}^g$	$\lambda_{em}{}^h$ (nm)	$\Phi_F{}^i$
1	0	83.0 (1a)	5320	1.6	0 (0)	395	185	0.19	505	0.01
2	0.5	85.3 (1b)	5820	1.7	11/45 (11/45)	378	182	0.24	493	0.01
3	1.0	67.6 (1c)	3610	1.4	11/34 (11/23)	355	190	0.28	504	0.01
4	1.5	34.0 (1d)	3530	1.4	11/28 (11/16)	343	1140	0.32	499	0.01

[a] By the homopolymerization of diyne 2 or the copolymerizations of 2 with 1-octyne 3 catalyzed by TaCl₅−Ph₄Sn in toluene at room temperature in an atmosphere of dry nitrogen for 24 h; [2] = 0.072 M, [TaCl₅] = [Ph₄Sn] = 20 mM. [b] Molar ratio. [c] Estimated by GPC in THF relative to polystyrene. [d] Integrated areas of proton absorption peaks of pentyl (A_{pen}) and phenyl groups (A_{ph}); data given in the parentheses are the theoretic ratios of the pentyl protons to the aromatic and acetylenic protons calculated from the monomer feed ratios. [e] Temperature for 5% weight loss (TGA, under nitrogen, heating rate: 20 °C/min). [f] Optical limiting threshold (incident fluence at which the nonlinear transmittance is 50% of the linear one). [g] Signal suppression (ratio of the saturated transmitted fluence to the maximum incident fluence). [h] Emission maximum (in THF). [i] Quantum yield of fluorescence (using 9,10-diphenylanthracene as standard).

geometry of the silacyclopentadiene ring in **2** matches those found in the CSD database.[14] The silole ring carbons C10−C20 and C30−C40 have characteristic double-bond lengths of 1.353(3)−1.365(3) Å. The exocyclic ethynyl groups have typical triple-bond lengths of 1.182(3)−1.185(2) Å, whose geometry is essentially linear, with Si1−C1(3)−C2(4) angles close to 180°. Silole **2** has a planar silacyclopentadiene ring, with torsion angles ≤3.3°. The phenyl substituents on the silole ring are typically twisted out of the silacyclopentadiene plane, with smaller torsion angles for the phenyl groups next to the silicon [from −44.6(4)° to −31.8(3)°] and larger angles for the groups at the C20 and C30 positions [from −66.8(3)° to −58.2(3)°].

Polycyclotrimerization of **2** is effected by TaCl₅−Ph₄Sn in toluene at room temperature, which gives a hyperbranched polyarylene **1a** in a high yield (83.0%; Table 3, no. 1). Polymer **1a** is completely soluble in such common solvents as toluene, THF, chloroform, and dichloromethane, thanks to its highly branched molecular structure. The gel permeation chromatography (GPC) analysis (relative to linear polystyrene) gives a weight-average molecular weight of 5320. This value is probably considerably underestimated because of the hyperbranched nature of the polymer, coupled with its rigid molecular structure. In our previous studies on hyperbranched polymers,[10,11,15] the underestimation was as large as 7-fold,[11] and the actual or real molecular weight of **1a** thus could be much higher than the relative value estimated from the GPC analysis.

Copolycyclotrimerization of diyne **2** with monoyne **3** in a molar feed ratio [3]/[2] = 0.5 produces a copolymer (**1b**) with a similar molecular weight (5820), again in a high yield (85.3%; Table 3, no. 2). Increasing the feed ratio to 1.0 decreases the molecular weight of the resultant polymer, possibly due to the increased possibility of end-capping of the propagating branches by the monoyne molecules (Scheme 3). The cyclotrimer-

Scheme 3
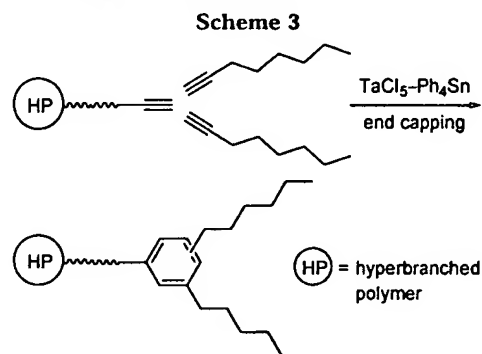
ization of an active branch carrying a triple-bond functional group with two triple bonds of two monoyne molecules would produce a "dead" benzene ring that ceases to propagate.[11] We envision that further increasing the molar feed ratio will further decrease the molecular weight of the polymer as well as its yield; this is confirmed by the polymerization data given in Table 3 (no. 4). Like the homopolymer (**1a**), all of the copolymers (**1b−1d**) are also soluble and processable, forming thin films upon spin-coating their solutions onto solid substrates.

Characterization of Molecular Structures. The structures of the polymers were characterized by spectroscopic methods. An example of the IR spectrum of polymer **1b** is shown in Figure 2; in the same figure, the spectrum of its monomer **2** is also given for comparison. The ≡C−H and C≡C stretching vibrations of **2** occur at 3252 and 2038 cm⁻¹, respectively. These acetylenic bands are not observed in the spectrum of **1b**, indicating that the hyperbranched polymer contains no acetylene groups. The triple bonds may have been exhausted by the cyclotrimerization reactions, or in other words, the alkyne building blocks have been consumed in the construction processes of the aromatic cores (Scheme 1) and peripheries (Scheme 3).
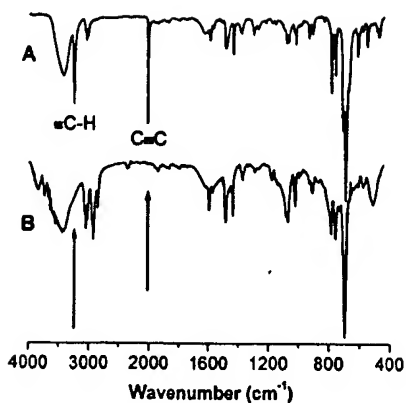
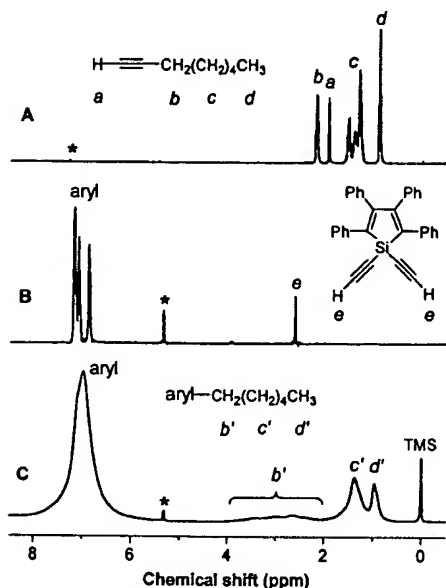Figure 2. IR spectra of (A) silolyldiyne 2 and (B) its polymer 1b.

Figure 3. ¹H NMR spectra of (A) 1-octyne 3 (in CDCl₃), (B) silolyldiyne 2 (in CD₂Cl₂), and (C) their polymer 1b (in CD₂-Cl₂). The solvent peaks are marked with *.

The acetylenic protons of monoyne 3 (a; Figure 3A) and diyne 2 (e; Figure 3B) resonate at δ 1.92 and 2.60, respectively. These peaks are not observed in the spectrum of polymer 1b (Figure 3C). The alkyne poly-cyclotrimerization converts the acetylenic triple bonds to aromatic rings, giving a strong absorption peak of aryl protons in the downfield region. The aryl absorption peak is, however, totally structureless, preventing us from estimating the isomeric ratio of the 1,2,4- and 1,3,5-conformers of the polymer.[10,11] Accompanying the polycyclotrimerization, the propargyl protons (b) of 1-octyne (3) are transformed to the benzyl ones (b') of 1b and the proton resonance is shifted downfield accordingly.[16] The resonance signals of the benzyl protons are very weak, spreading over a wide spectral range (δ 2–4), because the protons are located in the immediate neighborhood of the rigid aryl rings.[10,11,16] Similar phenomena have been observed in our linear polyacetylene and hyperbranched poly(ferrocenylenesilyne) systems: the absorption "peaks" of the allylic protons in the vicinity of the stiff polyacetylene backbones (=C–CH₂),[17] and the methylene protons next to the rigid ferrocene rings (Fc–CH₂)[15] are also very weak and broad and sometimes undetectable.
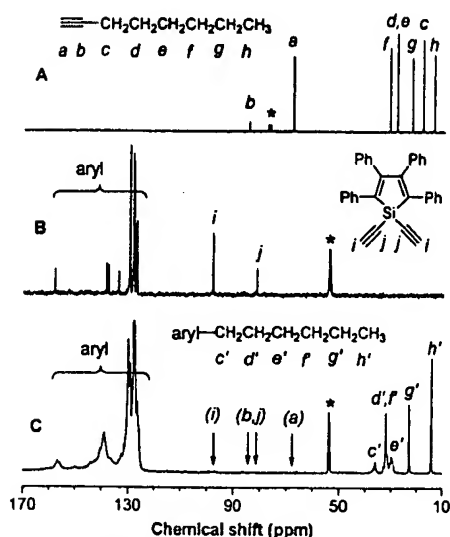

Figure 4. ¹³C NMR spectra of (A) 1-octyne 3 (in CDCl₃), (B) silolyldiyne 2 (in CD₂Cl₂), and (C) their polymer 1b (in CD₂-Cl₂). The solvent peaks are marked with *.

The two partially overlapping peaks in the spectral region of δ 0.5–2 (c' and d') are unambiguously due to the resonance of the aliphatic protons of the pentyl group originally from 1-octyne (3), while the strong single peak in the downfield region of δ ~ 6–8 is the sum of the absorptions of the aromatic protons of the "old" phenyl rings of diyne 2 and the "new" ones formed by the cyclotrimerizations. The ratio of the integrated areas of absorption peaks of the pentyl (A_{pen}) and phenyl protons (A_{ph}) for 1b is 11/45, coinciding with the theoretical value calculated from the molar ratio ([3]/[2] = 0.5 or 1/2) of the monomer feed (Table 3, no. 2). This suggests that in this case the cyclization process involves an average of one (1) molecule of monoyne 3 and two (2) molecules of diyne 2. When the feed ratio is increased, the theoretical A_{pen}/A_{ph} value increases rapidly, although the experimental one increases much slowly. When the feed ratio is increased to 1.5, the experimental value (11/28) becomes very different from the theoretical one (11/16). This is not surprising because if the reaction had proceeded according to the exact stoichiometry of the monomer feed mixture, no polymer products would have been formed. The difference between the experimental and theoretical values suggests that many monoyne molecules have been consumed by their self-cyclotrimerizations into low molecular weight benzene derivatives of 1,2,4- and/or 1,3,5-trihexylbenzenes,[10,11] which were washed away during the purification processes of the polymeric product. The higher relative ratio of the monoyne moiety in polymer 1d (11/28 or 39%), in comparison to that in 1b (11/45 or 24%), indicates that a larger amount of 1-octyne 3 has been incorporated into the structure of 1d. In other words, the end-capping reaction (Scheme 3) is more active when the feed ratio is increased. The active termination should decrease the molecular weight of the polymer as well as its yield, in agreement with the experimental results.

Figure 4 shows the ¹³C NMR spectra of monoyne 3, diyne 2, and polymer 1b. The acetylenic carbons of 1-octyne (3) absorb at δ 84.6 and 68.0, while those of 2 resonate at δ 97.6 and 81.4. All of these acetylenic peaks disappear in the spectrum of 1b, again confirming that the triple bonds have been consumed by the cyclotrim-
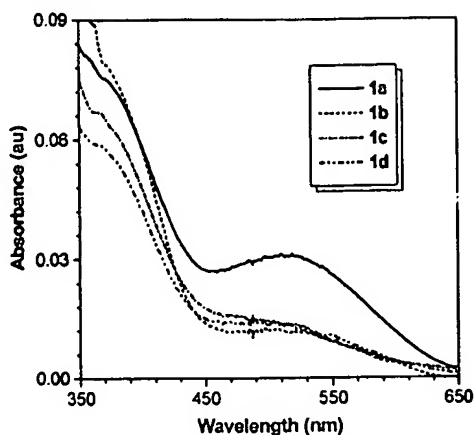
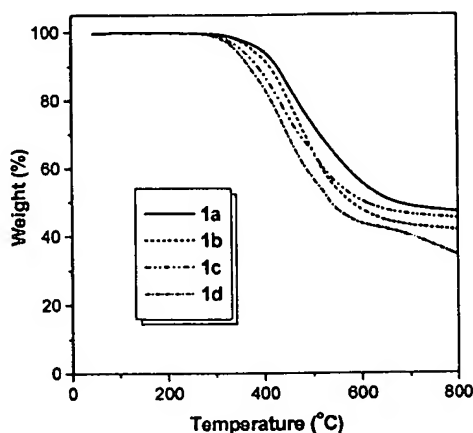**Figure 5.** UV spectra of THF solutions (10 μg/mL) of hyperbranched poly(phenylenesilolene)s.

Figure 6. TGA thermograms of hyperbranched poly(phenylenesilolene)s.
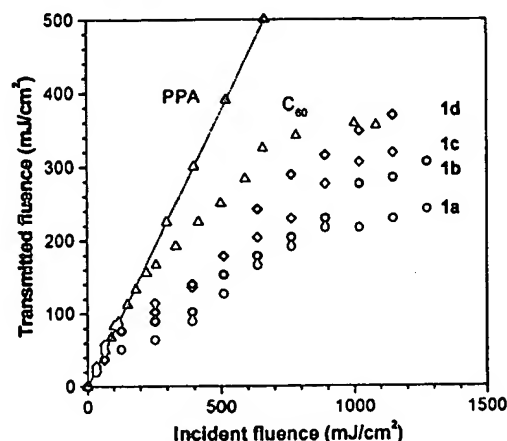

Figure 7. Optical responses to 8 ns, 10 Hz pulses of 532 nm laser light, of dichloromethane solutions (0.70 mg/mL) of hyperbranched poly(phenylenesilolene)s. Data for poly(phenylacetylene) (PPA) and C_{60} solutions are shown for comparison. Linear transmittance (%): 70 (**1a**), 80 (**1b**), 82 (**1c**), 85 (**1d**), 79 (C_{60}), 75 (PPA).

erization reactions. The propargyl carbon of 1-octyne exhibits a strong, sharp resonance peak (*c*) in Figure 4A, which is, however, absent in the spectrum of **1b**. The propargyl peak is replaced by a weak, broad benzylic peak (*c'*) in the downfield region (Figure 4C) due to cyclization.[10,11]

The siloles absorb in the UV spectral region ($\lambda_{max} \sim$ 378 nm).[3,4,8] All of the hyperbranched polymers, however, absorb in the visible region (Figure 5). The polymers thus must possess extended conjugation, possibly due to the synergistic interplay of the $\sigma-\pi$ conjugation of the silole rings and the electronic communication of the aromatic rings via the silicon bridges.[1,15,18] Homopolymer **1a** is the most conjugated on the basis of its strongest absorption in the visible ($\lambda_{max} \sim$ 520 nm). All three copolymers (**1b**–**1d**) are less conjugated, probably due to the incorporation of nonconjugating 1-alkyne moieties into the macromolecular structures.

Thermal and Optical Stabilities. All of the silole-containing hyperbranched polymers are thermally stable: no weight losses are detected by the TGA analyses when the polymers are heated to ~300 °C (Figure 6). About half of their original weights remain when the polymers are heated to ~800 °C; that is, the polymers graphitize or ceramize upon pyrolysis. The temperatures for 5% weight loss (T_d's) for the polymers are given in Table 3. The thermal stability of the polymers decreases with increasing monoyne component. Thus, the T_d of **1a**, which contains no monoyne

moieties, is as high as 395 °C, while the T_d of **1d**, which has the highest content of monoyne moieties, decreases to 343 °C. This is easy to understand: the incorporation of the weak aliphatic moieties into the copolymers should enhance their thermolytic susceptibility, and the copolymers should thus decompose at lower temperatures.

The hyperbranched polymers are also optically stable. Figure 7 shows the optical responses of the polymer solutions to 532 nm laser pulses, along with the data for the solutions of poly(phenylacetylene) (PPA)[19] and C_{60}.[20] The transmitted fluence of PPA, a linear acetylenic polymer, linearly increases with an increase in the incident influence (linear transmittance $T =$ 75%). The hyperbranched polyarylenes show comparable linear transmittance in the low-fluence region ($T =$ 70–85%) but become opaque in the high-fluence region. The polymers strongly attenuate the power of the intense laser pulses, whose optical limiting performances are superior to that of C_{60}, the best-known optical limiter.[20-22] Among the hyperbranched polymers, **1a** exhibits the best performance, which starts to limit the optical power at a low threshold (185 mJ/cm²) and suppresses the optical signals to a great extent (19%; Table 3, no. 1). The optical limiting properties decrease when the content of the nonconjugated 1-alkyne moieties is increased in the hyperbranched polymer (although their performances are still better than that of C_{60}). The high degree of electronic conjugation in **1a** (cf. Figure 5) may be responsible for its high optical nonlinearity.

Cooling-Enhanced Light Emission. The dilute solutions (10 μg/mL) of the hyperbranched polymers emit blue-green light peaked at ~500 nm when excited at 407 nm (Figure 8). The photoluminescence spectrum of the polymer blue shifts from **1a** to **1d**, probably due to the difference in the degree of conjugation of the polymers. In our previous study, we found that the polyacetylenes prepared from the metathesis polymerizations of silolylmonoynes (Chart 2) were nonemissive when molecularly dissolved in dilute solutions.[8] As shown in Figure 8, polymers **1a**–**1d** are photoluminescent, even when they are molecularly dissolved. This difference in photoluminescence behavior between polymers **1a**–**1d** and the polyacetylenes rules out the possibility that silolyldiyne **2** underwent alkyne me-
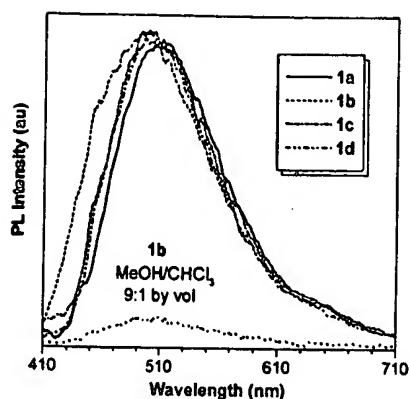
Figure 8. Photoluminescence spectra of hyperbranched poly-(phenylenesilolene)s **1a–1d** in THF and **1b** in a methanol/chloroform mixture (9:1 by volume) at room temperature; [1] = 10 μg/mL, λ_{ex} = 407 nm.
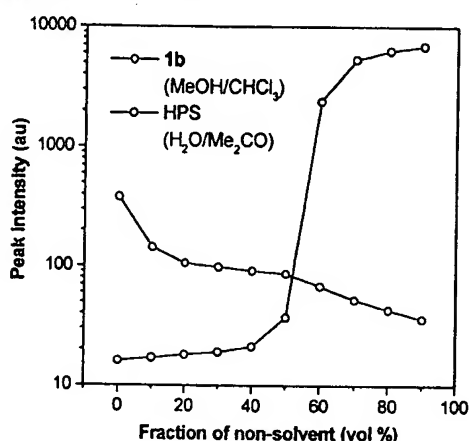

Figure 9. Peak intensity of photoluminescence of **1b** vs solvent composition of methanol/chloroform mixture at room temperature; [1b] = 10 μM, λ_{ex} = 407 nm. Data for 1,2,3,4,5,6-hexaphenylsilole (HPS) in water/acetone mixtures are shown for comparison.

tathesis polymerization or that polymers **1a–1d** possess a linear polyacetylene structure.[23]

Compared to low molecular weight silole analogues, the hyperbranched polymers are more luminescent [Φ_F = 1% for the polymer (Table 3) vs $\Phi_F \leq 0.1\%$ for the siloles[3,4,14,24]]. In general, however, the polymers are still weak emitters. As discussed in the Introduction section, the emission of the silole molecules can be enhanced by aggregation (AIE)[3,8] and cooling (CCE).[8,14] We first checked whether the luminescence of the polymers could be enhanced by aggregate formation by adding nonsolvents to their dilute solutions. The polymer emission is, however, gradually weakened, instead of being intensified, when methanol is progressively added to the polymer solutions, as exemplified by the data shown in Figures 8 and 9 for polymer **1b**. In contrast, when similar amounts of a nonsolvent (water) are added to an acetone solution of HPS (Chart 2), a silole analogue of **1b**, its photoluminescence intensity is enhanced by up to ~400 times (Figure 9)! In our previous study, we found that when the silole pendants were directly attached to the rigid linear polyacetylene backbone, the resultant polymer (PSA in Chart 2) was AIE-inactive.[8] In this study, the silole rings are put into the rigid hyperbranched polyphenylene structure, and the resultant polymers are again AIE-inactive. The stiff polyene
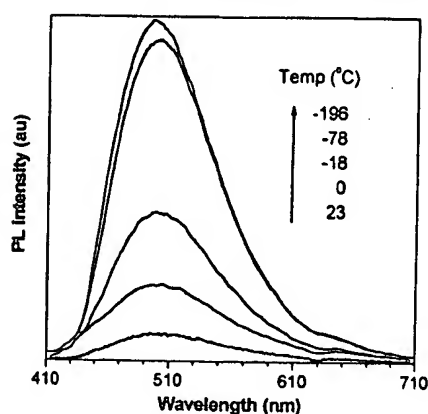

Figure 10. Photoluminescence spectra of **1b** in dioxane at different temperatures; [1b] = 10 μM, λ_{ex} = 407 nm.
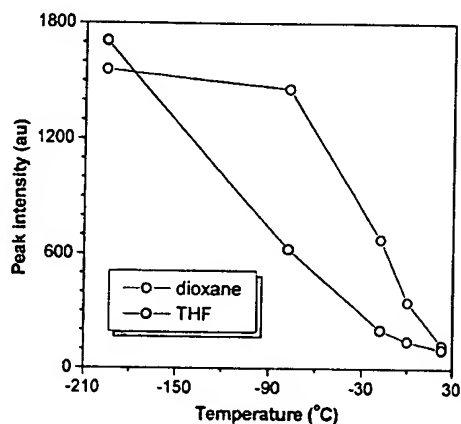

Figure 11. Effect of temperature on the peak intensity of the photoluminescence of **1b** in dioxane and THF; [1b] = 10 μM, λ_{ex} = 407 nm.

rods and the hard polyarylene balls may have randomly piled up when they aggregate in the poor solvent environments. Such chaotic stacks of the rigid polymers may generate large free volumes in the aggregates,[25,26] in which the phenyl rings may still be able to rotate round the axes of the single bonds linked to the silacyclopentadiene core. Such intramolecular interactions may have nonradiatively deactivated the excited species[27] and hence quenched the silole emission, as discussed in our previous papers.[8,14]

We then checked whether the photoluminescence of polymers could be enhanced by cooling. When a dilute dioxane solution of polymer **1b** is cooled, its photoluminescence intensity increases (Figure 10). This is because the intramolecular rotations of the phenyl rings round the axes of the silacyclopentadiene core are impeded at the low temperatures, which blocks the radiationless channel and populates the radiative decay of the excitons.[8,14] The spectral profile hardly changes with temperature, suggesting that the photoluminescence is still associated with the radiative decay of the singlet excitons[4] but not their triplet counterparts. The photoluminescence intensity increases rapidly when the polymer solution is cooled from 23 to −78 °C but levels off when further cooled to −196 °C (Figure 11). Dioxane has a melting point of 11.8 °C, and decreasing temperature would rapidly increase the solvent viscosity and vitrify the polymer solution. The void spaces of the polymer aggregates would be filled by the frozen solvent molecules and the intramolecular rotations of the silole

moieties would be hampered by the glassy surrounding, thus leading to the rapid increase in the photoluminescence intensity.[8] At −78 °C, the whole solution may have already become a densely packed solid, and further cooling thus causes little change in the light emission.

The cooling effect on the THF solution of **1b** is different from that on its dioxane solution (Figure 11). Upon cooling, the photoluminescence intensity again increases but at a slower rate. THF is a liquid with a high solvating power but a low melting point (−108 °C), which can keep the polymer in solution at much lower temperatures. When cooled to −78 °C, the solvent is still in the liquid state and the solute should still be molecularly dissolved. The photoluminescence enhancement with temperature thus should be caused by the restricted intramolecular rotations due to pure cooling effect but no "glassy" effect. Because of this, the photoluminescence intensities of the THF solution are weaker than those of the dioxane solution or glass in the temperature region of 23 to −78 °C. Further cooling to −196 °C freezes the THF solvent and brings the photoluminescence intensity of the polymer in the THF glass to a level comparable to that in the dioxane glass.

Concluding Remarks

The silole ring, an organometallic chromophore with novel luminescence properties, is successfully incorporated into a hyperbranched polyphenylene structure through the facile polycyclotrimerizations of alkynes catalyzed by a transition-metal mixture of $TaCl_5$−Ph_4-Sn under mild reaction conditions. The silole units are interconnected through the formation of trisubstituted benzenes, or the silolyl rings are linked together by the phenyl rings in the three-dimensional space. This unique molecular structure endows **1** with an array of interesting properties: the hyperbranched polymers are readily processable (completely soluble), thermally stable (T_d up to ∼400 °C), electronically conjugated (λ_{max} ∼ 520 nm), nonlinear optically active (F_L ∼ 180 mJ/cm²), and highly emissive upon excitation at low temperatures (cooling-enhanced emission).

The linear optical transmittance of the polymer solutions is comparable to, or higher than, that of the C_{60} solutions, but the optical limiting thresholds and signal suppression ratios of the former are superior to those of the latter. In other words, the hyperbranched polyphenylenes are better optical limiters than C_{60}. Noting that the fullerene is a three-dimensionally conjugated buckyball, the three-dimensionally conjugated electronic structure of the hyperbranched polyphenylenes may be responsible for their optical nonlinearity, although the detailed optical limiting mechanism awaits further investigation.

The light emission of **1** is sensitive to temperature change: the photoluminescence intensities of the polymer solutions increase when temperatures are decreased. The cooling-enhanced emission of **1** is probably caused by the restricted intramolecular rotations of the phenyl rings upon the axes of the single bonds linked to the silole cores. This is a thermally modulated photonic process and can be regarded as a special type of thermochromism,[28] offering a versatile means for tuning the photoluminescence of the hyperbranched polymers.

Experimental Section

Materials. Tetrahydrofuran and 1,4-dioxane (Aldrich) were predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine (RdH) was distilled from KOH. Tolane (98%), silicon(IV) chloride (99%), lithium metal wire (99.9%), 1-octyne (3; 97%), ethynylmagnesium bromide (0.5 M in THF), tantalum(V) chloride (99.8%), and tetraphenyltin (97%) were all purchased from Aldrich and used as received without further purification.

Instrumentation. The molecular weights of the polymers were estimated by GPC using a Waters Associates liquid chromatograph equipped with a Waters 510 HPLC pump, a Rheodyne 7725i injector with a stand kit, a set of three Styragel columns [HT3 (effective molecular weight range: 500−30 × 10³), HT4 (5 × 10³−600 × 10³), and HT6 (200 × 10³−10 × 10⁶)], a column temperature controller, a Waters 486 wavelength-tunable UV−vis detector, a Waters 410 differential refractometer (RI detector), and a system DMM/ scanner with eight-channel scanner option. All the polymer solutions were prepared in THF (∼2 mg/mL) and filtered through 0.45 μm PTFE syringe-type filters before being injected into the GPC system. THF was used as eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 40 °C, and the working wavelength of the UV detector was set at 254 nm. A set of 12 monodisperse polystyrene standards (Waters Associates) covering a molecular weight range of 982−1945300 was used as calibration references.

The ^{1}H and ^{13}C NMR spectra were obtained on a JEOL 400 or a Varian Mercury 300 using TMS (tetramethylsilane) as internal reference. The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer using KBr pellets. The mass spectra were measured on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. The UV−vis spectra were obtained on a Milton Roy Spectronic 3000 array spectrophotometer. The thermal stability of the polymers was evaluated on a Perkin-Elmer thermogravimetric analyzer TGA 7 under nitrogen at a heating rate of 20 °C/min. The photoluminescence spectra of the silole solutions and aggregates were recorded on a SLM 8000C spectrofluorometer.

The X-ray diffraction intensity data were collected from a suitable specimen of 0.35 × 0.25 × 0.15 mm dimension on a Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation at 100 K. The crystal structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on F^2 by using the Bruker SHELXTL (version 6.10) program package. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in ideal positions and refined as riding atoms.

The optical limiting experiments were carried out at 532 nm, using 8 ns optical pulses generated from a frequency-doubled Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near-Gaussion transverse mode with a repetition rate of 10 Hz. The pulsed laser beam was focused onto a 1 cm square quartz cell filled with a polymer solution in dichloromethane. The incident and transmitted energies were measured by an OPHIR detector (30-A-Diff-SH), and every point of the optical limiting data was the average of at least 15 laser shots. The detector was connected to a computer before and after the optical limiting data were taken, and the output stability of the laser equipment was double checked by taking a series of output data by the energy meter every 10 s for an extended period of time.

Synthesis. The silolyldiyne monomer (2) was prepared by the reaction of 1,1-dichloro-2,3,4,5-tetraphenylsilole (6) with ethynylmagnesium bromide (Scheme 2). The detailed synthetic procedures are given below.

1,1-Dichloro-2,3,4,5-tetraphenylsilole (6). Under dry nitrogen, 180 mg of freshly cut lithium shavings (25.9 mmol) was added to a solution of tolane (4; 5.99 g, 33.6 mmol) in 25 mL of THF. The mixture was stirred for 12 h at room temperature and was then added dropwise to a solution of silicon(IV) chloride (1.33 mL, 11.6 mmol) in 120 mL of THF. The solution was stirred for 2 h at room temperature and then refluxed for 5 h at evaluated temperature. The product (6) was used in

situ as a starting material for the preparation of **2** without isolation.

1,1-Diethynyl-2,3,4,5-tetraphenylsilole (2). Into the above THF solution of **6** at room temperature was dropwise added 46.4 mL of 0.5 M THF solution of ethynylmagnesium bromide (23.2 mmol). After stirring for 2 h, the mixture was filtered, and the crude product was purified on a silica gel column using a hexane/chloroform mixture (2:1 by volume) as eluent. A yellow-greenish solid of **2** was isolated in 30% yield (1.5 g) based on silicon(IV) chloride. Recrystallization from toluene/heptane solution gave 1.2 g of pure product (24% yield based on silicon(IV) chloride); mp 199–201 °C. IR (KBr), v (cm^{-1}): 3252 (≡C–H stretch), 2038 (C≡C stretch). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.20–7.01 (m, br, 16H, Ar), 6.81 (m, 4H, Ar), 2.60 (s, 2H, ≡CH). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 157.4 (C=C–Si), 138.0 (ipso-Ar), 137.2, 133.5, 129.5, 129.4, 128.0, 127.7, 126.9 (*m*-, *p*-, *o*-Ar), 126.5 (=C–Si), 97.6 (≡CH), 81.5 (Si–C≡). MS (CI): *m/e* 435 [(M + 1)$^+$]. UV (CHCl$_3$, 4.0 × 10^{-5} mol/L), λ_{max} (nm)/ϵ_{max} (mol^{-1} L cm^{-1}): 247/2.35 × 10^4, 378/9.27 × 10^3.

Polymerization. All of the polymerization reactions and manipulations were carried out under dry nitrogen using a standard Schlenk technique in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was conducted in air. A typical procedure for the copolymerization of **2** with 1-octyne **3** is given below.

Into a thoroughly baked and moisture excluded Schlenk tube were placed 18.0 mg of TaCl$_5$ (0.05 mmol) and 21.3 mg of Ph$_4$Sn (0.05 mmol) in a glovebox. The catalyst mixture was dissolved in 1.0 mL of toluene and aged at room temperature for 15 min. A solution of 78.1 mg (0.18 mmol) of **2** and 13.3 mL (0.09 mmol) of **3** in 1.5 mL toluene was then added dropwise into the catalyst solution. After stirring at room temperature for 24 h, the reaction was quenched by the addition of a small amount of methanol. The polymer solution was dropped into 250 mL of methanol via a cotton filter while stirring. A deep purple powder of **1b** was isolated in 85.3% yield (75.1 mg). M_w 5820; M_w/M_n 1.7 (GPC, Table 1, no. 2). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$), δ (TMS, ppm): 6.90 (br, Ar), 2.54 (br, Ar–C*H*$_2$), 1.30 (CH$_2$), 0.91 (CH$_3$). ^{13}C NMR (400 MHz, CD$_2$-Cl$_2$), δ (TMS, ppm): 156.8 (C=C–Si), 138.9 (ipso-Ar), 130.2–126.5 (*m*-, *o*-, *p*-Ar; =C–Si), 36.2 (Ar–CH$_2$), 32.1 (Ar–CH$_2$–CH$_2$ and CH$_2$–CH$_2$–CH$_3$), 29.8 (CH$_2$–CH$_2$–CH$_2$–CH$_3$), 23.0 (CH$_2$–CH$_3$), 14.3 (CH$_3$). UV (CHCl$_3$, 10 μM), λ_{max} (nm)/ϵ_{max} (mol^{-1} L cm^{-1}): 242/22 200, 368/3300 (sh), 521/567.

Supporting Information Available: Crystal structures with atom labels, tables of crystal data and intensity data, atomic coordinates, anisotropic displacement parameters, and bond distances and angles for silolyldiyne **2** as well as its cif file (CCDC 195947). This material is available free of charge via the Internet at http//pubs.acs.org.

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